

Modeling Secondary Zinc-Air Batteries with Advanced Aqueous Electrolytes

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Motivation

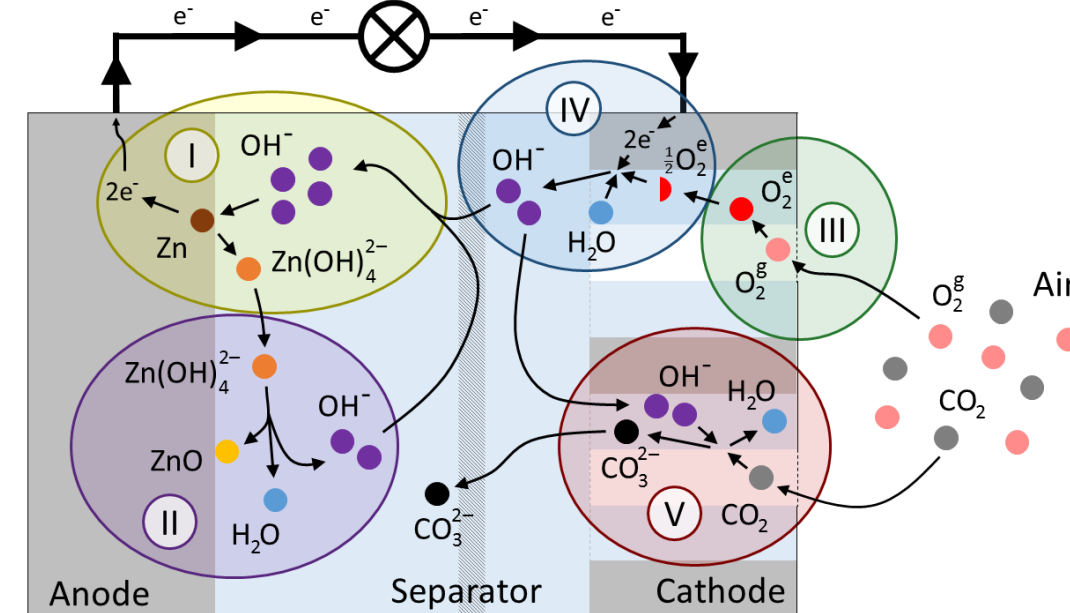
- Primary zinc-air battery commercially available
 - High specific energy, low cost, high operational safety
 - Hearing aid battery, e.g., VARTA PowerOne PR44
- Development of rechargeable zinc-air battery
 - Zinc dendrites, electrolyte carbonation, oxygen redox chemistry, anode passivation
 - Stationary energy storage
- Electrolytes: aqueous alkaline, aqueous near-neutral

Model: Alkaline Electrolyte

- 1D continuum model of alkaline zinc-air battery

- Chemical reactions:

- $\text{Zn} + 4\text{OH}^- \rightleftharpoons \text{Zn(OH)}_4^{2-} + 2\text{e}^-$
- $\text{Zn(OH)}_4^{2-} \rightleftharpoons \text{ZnO} + 2\text{OH}^- + \text{H}_2\text{O}$
- $\text{O}_2^g \rightleftharpoons \text{O}_2^l$
- $\frac{1}{2}\text{O}_2^l + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons 2\text{OH}^-$



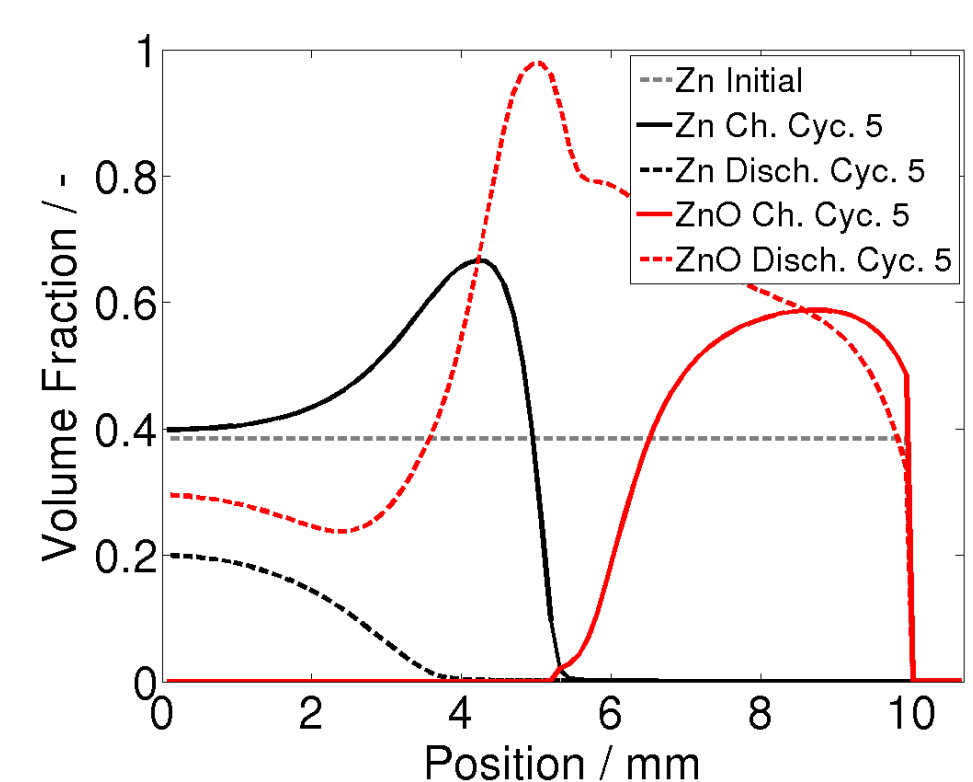
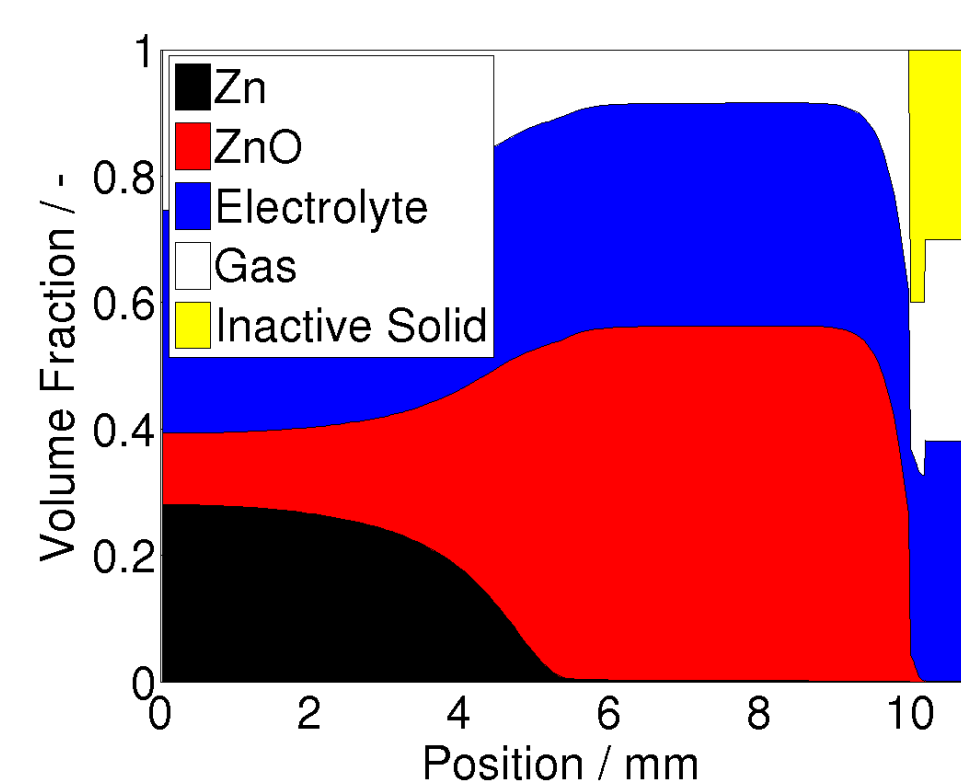
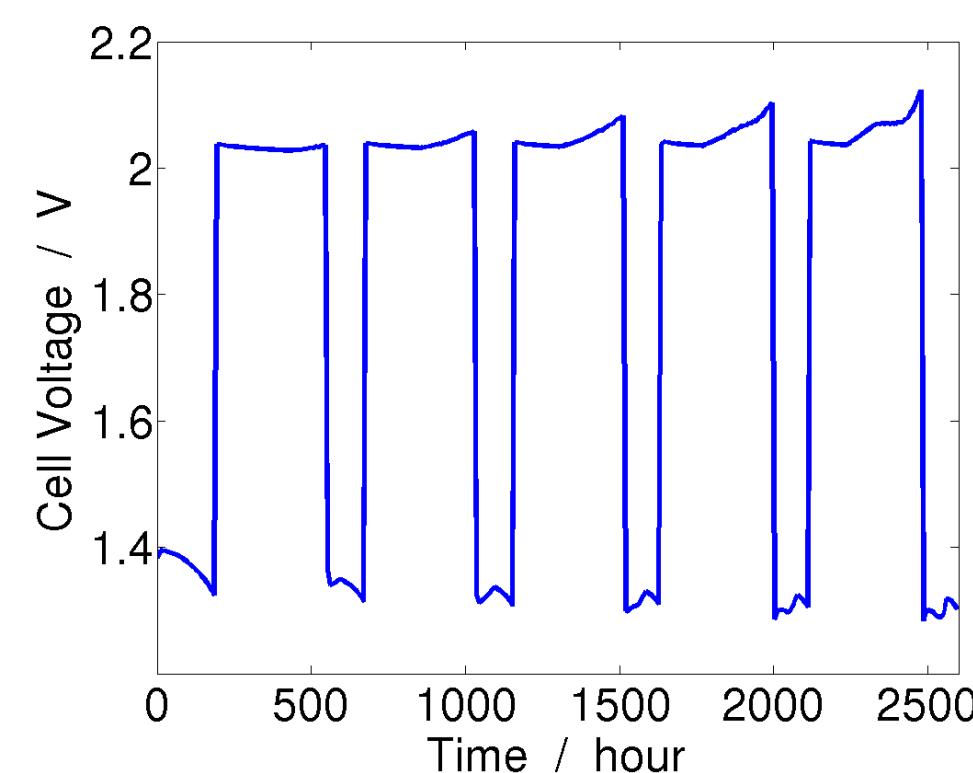
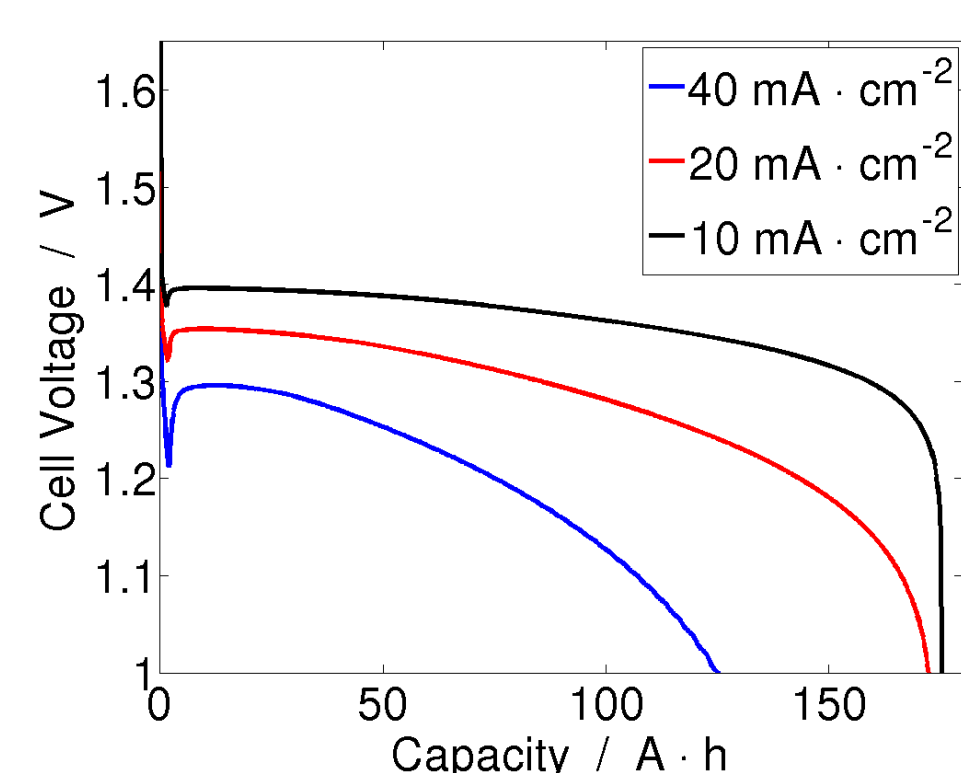
- Consistent transport: diffusion, migration, and convection

$$\partial_t (\epsilon_e^\beta c_i) = \vec{\nabla} \cdot (\epsilon_e^\beta D_i \vec{\nabla} c_i) + \vec{\nabla} \cdot \left(\epsilon_e^\beta \frac{t_i}{z_i F} \vec{j} \right) + \vec{\nabla} \cdot (\epsilon_e^\beta c_i \vec{v}_e) + S_i$$

- Coexisting gas, liquid, and solid phases
- Cathode: hydrophobic gas diffusion electrode (GDE)
- Anode: spherical zinc particles, passivating ZnO shell
- Electrolyte: aqueous KOH solution

Simulations: Alkaline Electrolyte

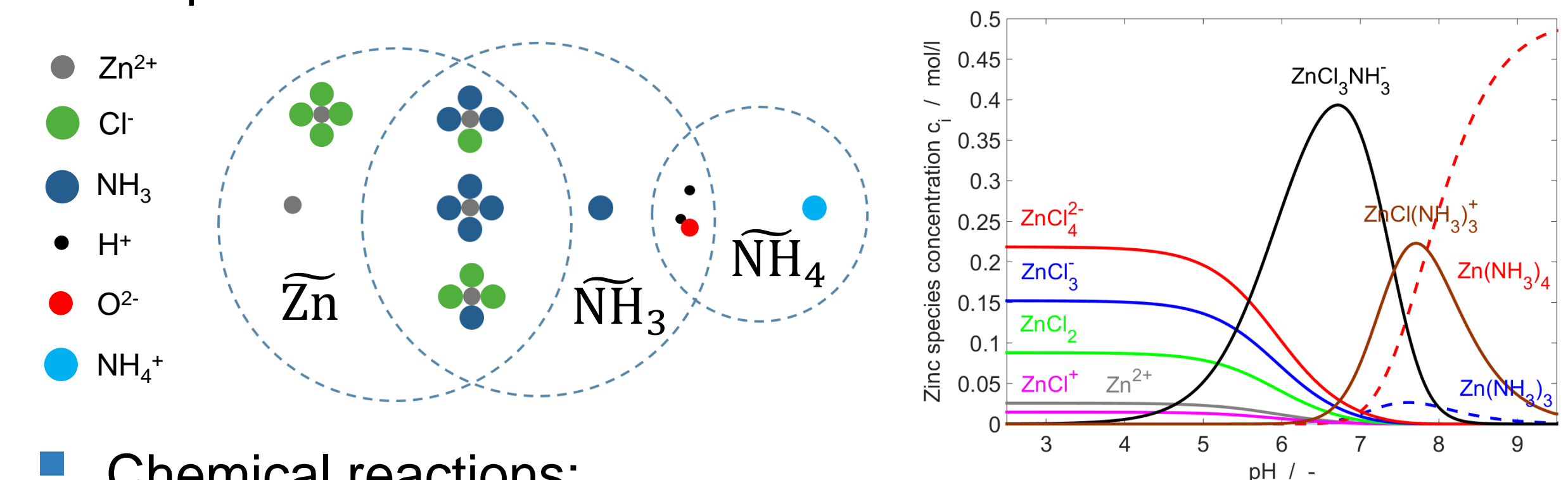
- Galvanostatic operation of prismatic zinc-air cell
 - Thick anode (10 mm), large energy capacity
 - Long reactant transport path and pore blockage with ZnO
 - Cell performance limited by mass transport



- ZnO precipitates first at the separator
 - Non-reactive zone creates barrier for KOH transport
 - Zinc electrode shape change during cycling

Model: Neutral Electrolyte

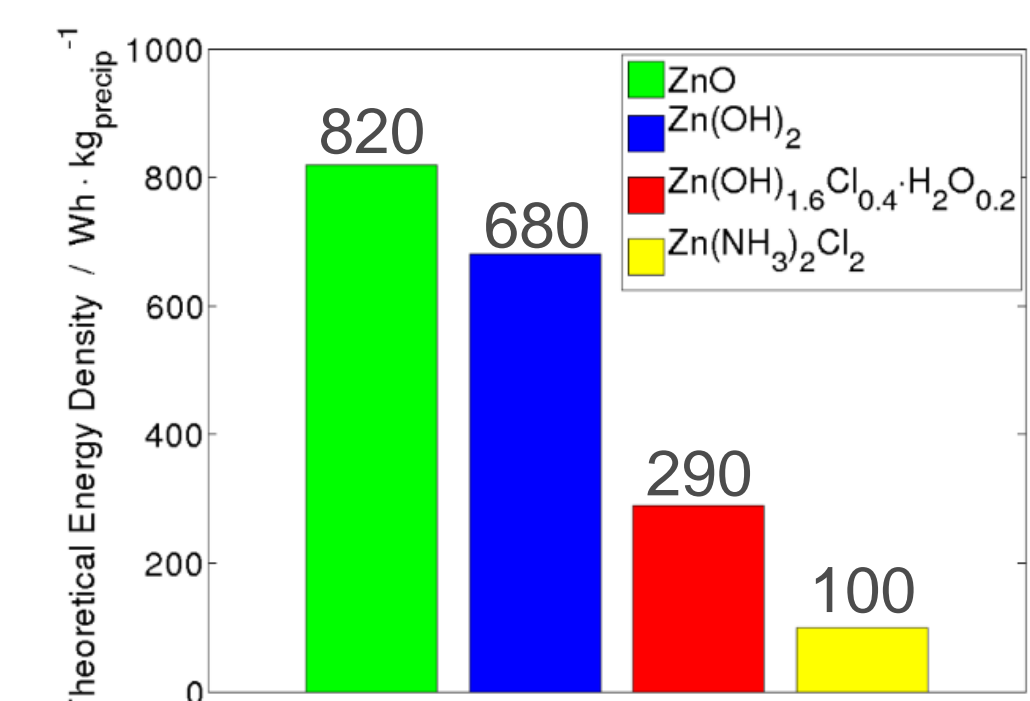
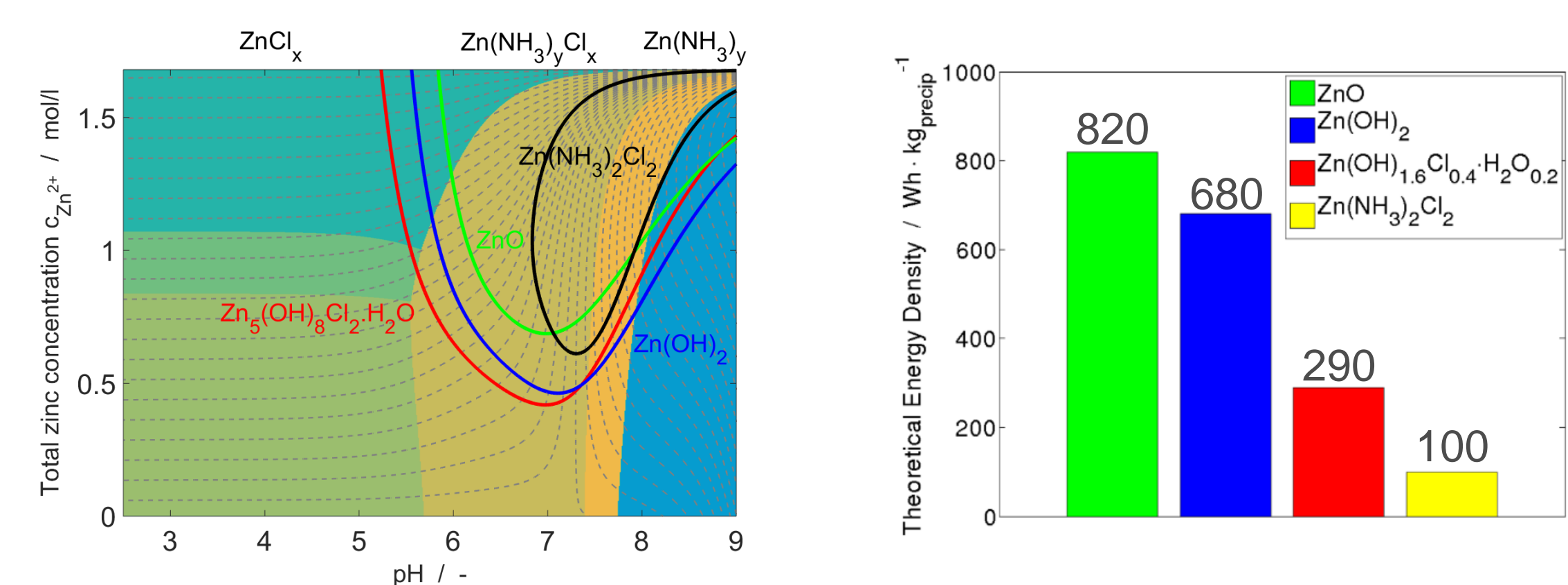
- $\text{NH}_4\text{Cl} + \text{ZnCl}_2$ electrolyte
 - No carbonation effects, improved cycling stability
- Zinc forms complexes with chlorine, ammonia, and hydroxide
 - Dominant aqueous species shifts with pH and composition
- System modelled with quasi-particles of conserved quantities:



- Chemical reactions:

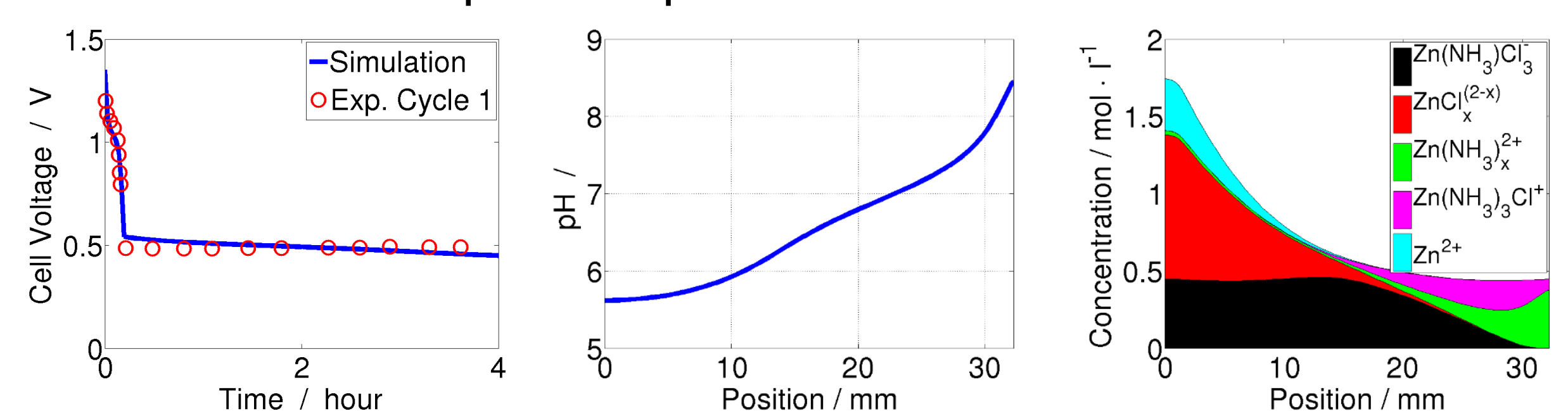
- $\text{Zn} \rightleftharpoons \text{Zn}^{2+} + 2\text{e}^-$
- $5\text{Zn}^{2+} + 8\text{NH}_3 + 2\text{Cl}^- + \text{H}_2\text{O} \rightleftharpoons \text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O} + 8\text{NH}_4^+$
- $\text{O}_2^g \rightleftharpoons \text{O}_2^l$
- $\frac{1}{2}\text{O}_2^l + 2\text{NH}_4^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O} + 2\text{NH}_3$

- Final discharge product determined by electrolyte composition and pH:



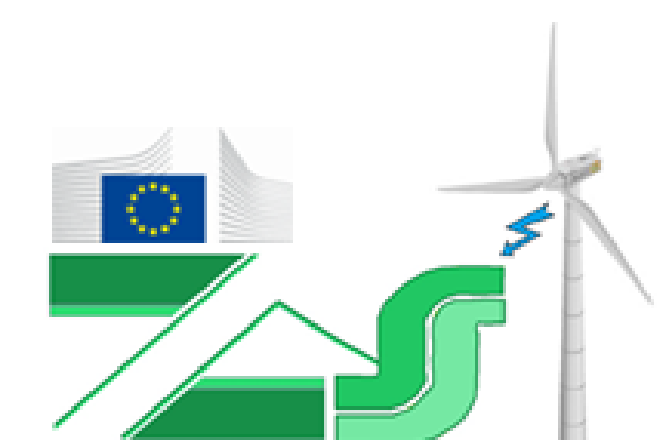
Simulations: Neutral Electrolyte

- Galvanostatic discharge at $5 \text{ mA} \cdot \text{cm}^{-2}$
- Initial potential drop due to reduction of MnO_2 catalyst
- Thick separator (30 mm)
 - Long transport path causes gradient in pH
 - Dominant aqueous species shifts across the cell



Conclusions

- Zinc-air: promising technology with long history
- Challenges:
 - Carbonation of alkaline electrolyte
 - Efficient and reversible oxygen reaction
 - Stable and reversible zinc deposition
 - Efficient electrolyte transport
- Development
 - Neutral chloride aqueous electrolyte
 - Cell architecture optimization



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